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# Electrophilic Fluorination of Organoplatinum(II) Iodides: Iodine and Platinum Atoms as Competing Fluorination Sites

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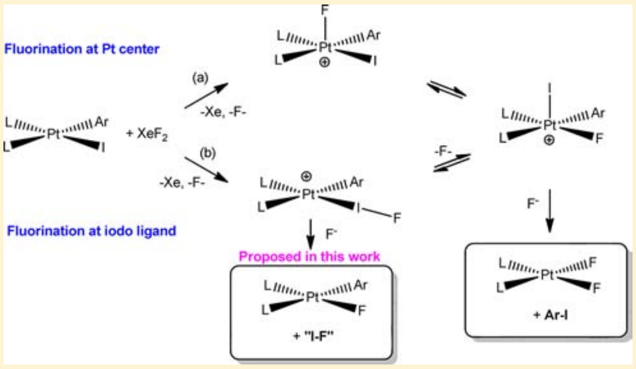
S Supporting Information

**ABSTRACT:** A series of diphosphine Pt(II) aryl iodo complexes were reacted with $XeF_2$ to cleanly produce the corresponding Pt(II) difluoro complexes and free iodoarenes. However, when aryl ligands bearing fluoro substituents in the ortho positions were used, the formation of the corresponding Pt(II) aryl fluoro complexes was observed in the reaction with $XeF_2$. In the case of the Pt$-C_6F_5$ complex, the products of the fluoride-for-iodide exchange were the only products observed by means of $^{31}$P and $^{19}$F NMR spectroscopy. The experimental and theoretical studies suggest that the formation of iodine−fluorine bond may accompany this transformation. The plausible "I−F" species could be trapped by electron-richer organoplatinum complexes to give a Pt(IV) transient which subsequently eliminates the corresponding aryl iodide. Hence, in some cases a pathway involving an attack of $XeF_2$ at the iodo ligand of Pt(II) aryl iodo complexes to generate I−F species can be operative in addition to or instead of the $XeF_2$ attack at the metal center. Our DFT studies demonstrate that the electrophilic attacks of $XeF_2$ at both sites, platinum and iodide, can be competitive.

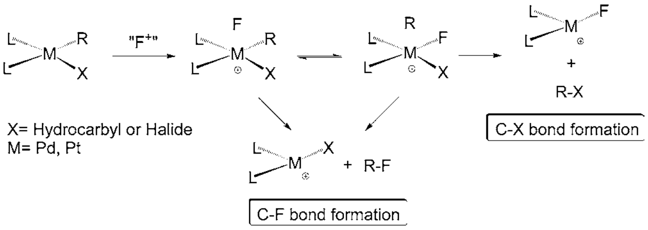


## INTRODUCTION

In recent years, the electrophilic fluorination of organometallic complexes became an important area of research.[1−4] The major driving force behind this expansion is the central role of organofluorine compounds in the development of new pharmaceuticals and agrochemicals.[5] The electrophilic fluorination can be viewed as a complementary tool to the commonly used nucleophilic fluorination techniques that allows for the direct conversion of C−H bonds into C−F bonds.[6−8] Electrophilic fluorination was also applied in the formation of the carbon−carbon bonds,[9] including the Ar$-CF_3$ bond,[10] as well as C−I bonds.[11] This last reaction was observed upon treatment of a series of (P∼P)Pd(II) aryl iodo complexes with $XeF_2$ and proceeded under very mild conditions giving the products, iodoarene and (P∼P)$PdF_2$, in a quantitative yield. The reaction was very general in scope and even (P∼P)Pd($C_6F_5$)I was found to be reactive, giving pentafluoroiodobenzene as the organic product.

The accepted general mechanism for the formation of new bonds under the electrophilic fluorination conditions is shown in Scheme 1. This mechanism involves the initial reaction of an electrophilic reagent acting as a source of "$F^+$" with the M(II) atom giving the M(IV) intermediate that undergoes subsequent reductive elimination[1,2] to produce the C−F, C−C, or C−X bonds.

**Scheme 1**



Notably, when an M(II) complex contains other relatively electron-rich atoms, such as an iodine atom at the metal center, the electrophilic fluorine might react with the coordinated halide. This reaction direction, known in the chemistry of organic iodides,[12] was not previously considered in organometallic chemistry. Herein, we present the first experimental and theoretical studies suggesting the formation of intermediates with a fluorine−iodine bond resulting from electrophilic fluorination with $XeF_2$ of Pt(II) aryl iodo complexes and discuss some potential implications of this reaction for group 10 organometallic chemistry.

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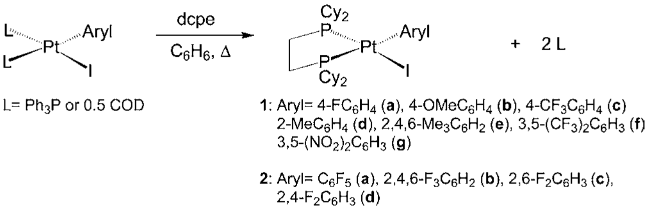
## RESULTS AND DISCUSSION

Complexes **1a–d,f,g** and **2b–d** were prepared following the standard procedures.[13] Typically, the corresponding $(Ph_3P)_2Pt(Ar)I$ was prepared by reacting $(Ph_3P)_4Pt$ with the corresponding iodoarene and treated with 1,2-dicyclohexylphosphinoethane (dcpe) in hot benzene for 24 h (Scheme 2). The products were obtained in 70–90% yields. In the case of **1e** and **2a**, (COD)Pt(Mes)I and $(COD)Pt(C_6F_5)I$ were used as the precursors, respectively. The $^{31}P$ NMR spectra of complexes **1** show two singlets with the $^{195}Pt$ satellites without the observed coupling due to the inequivalent phosphorus atoms in the mutual cis position. The presence of the ortho-F substituents in **2a–d** results in the splitting of the $^{31}P$ NMR signal of the phosphine ligand trans to the aryl group. This signal appears as a doublet in **2d**, triplet in **2b,c**, and multiplet (due to additional two meta-F atoms) in **2a** with $J_{FP}$'s of ~14 Hz.

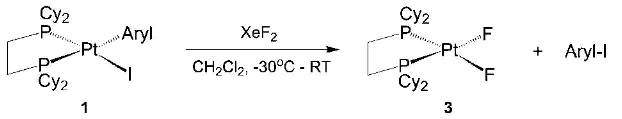
**Scheme 2**



The X-ray structure of **1e** (Figure 1a) shows the metal center in a square planar geometry. The bond angles at the Pt atom are close to the ideal 90°. Stronger trans influence of the mesityl group over iodide is manifested in a longer Pt(1)–P(4) distance of 2.3088(14) Å compared with 2.2455(14) Å for the Pt(1)–P(3) distance. The Pt(1)–I(2) bond length of 2.6570(4) Å compares well with other Pt–I distances in similar complexes.[14] The crystallographic features of complex **2b**, crystallized from $CH_2Cl_2$ (Figure 1b), are nearly identical to those in **1e**. The presence of the electron-withdrawing $2,4,6\text{-}F_3C_6H_2$ group has little effect on the bond lengths of the Pt center. For example, the Pt(1)–P(3) (trans to the aryl) and Pt(1)–P(4) bonds of 2.2908(18) and 2.2375(18) Å, respectively, correspond well to the platinum-phosphine distances in **1e**. Similarly, the Pt(1)–C(31) bond length of 2.086(7) Å in **2b** is insignificantly shorter than that in **1e** (2.093(5) Å). Yet, when compared with the bond distances in **2a** (Figure 1c), one can see a trend in the electron density influence on the bonds at the metal center. For instance, the Pt(1)–C(31) bond of 2.075(5) Å is again slightly shorter in **2a** than in **1e** and **2b**, and so is the Pt(1)–P(4) bond trans to the aryl of 2.2881(12) Å.

Upon reaction of complexes **1** with $XeF_2$ in $CH_2Cl_2$ at room temperature, their complete conversion to complex $(dcpe)Pt^{II}F_2$ (**3**) and the corresponding free iodoarenes was observed at room temperature (Scheme 3). The reactions proceeded rapidly with both electron-rich and electron-poor aryl derivatives, as well as with the sterically hindered ones (*o*-tolyl, **1d** or mesityl, **1e**). Cooling the reactions down to −78 °C did not enable us to find evidence for the involvement of any intermediates that could be detected by means of $^{19}F$ or $^{31}P$ NMR spectroscopy. In some cases, the formation of small amounts (<5%) of (dcpe)Pt(I)F (**4**) and (dcpe)Pt(Ar)F (**5**) complexes could be observed, likely as a result of the Pt(II) difluoro complexes acting as a source of a strongly nucleophilic $F^-$ anion.[15] Indeed, the addition of a $CH_2Cl_2$ solution of **3** to a solution of **1a** led to the formation of **4** and **5a** (eq 1).

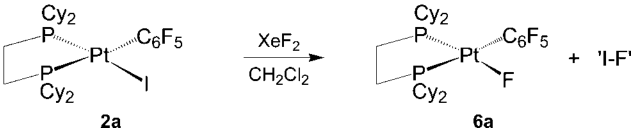
**Scheme 3**



$$\underset{(\mathbf{3})}{(dcpe)PtF_2} + \underset{(\mathbf{1a})}{(dcpe)Pt(4\text{-}FC_6H_4)I}$$
$$\rightarrow \underset{(\mathbf{4})}{(dcpe)Pt(I)F} + \underset{(\mathbf{5a})}{(dcpe)Pt(4\text{-}FC_6H_4)F} \qquad (1)$$

Interestingly, the addition of 1 equiv of $XeF_2$ to a solution of the pentafluorophenyl complex **2a** did not lead to the formation of either **3** or $C_6F_5$–I. Instead, the slightly yellowish solution turned dark pink and a nearly quantitative formation of the fluoro aryl complex **6a** was observed (Scheme 4). As in the

**Scheme 4**



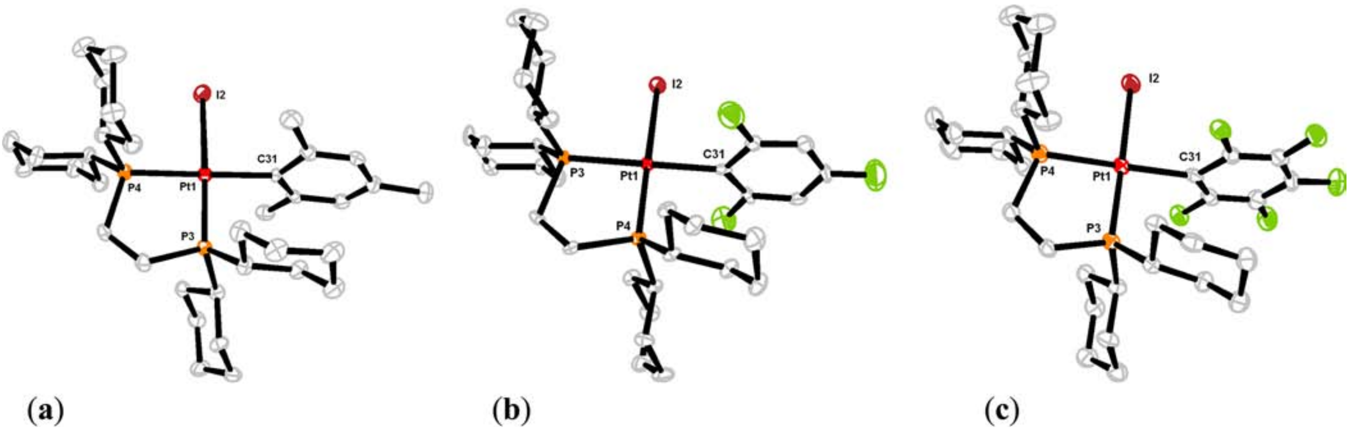


**Figure 1.** X-ray crystal structures of complexes **1e** (a), **2b** (b) and **2a** (c). Hydrogen atoms and solvent are omitted for clarity.

case of complexes **1**, the reaction with $XeF_2$ proceeded extremely fast even at −78 °C or just above the $CH_2Cl_2$ melting point (−96 °C). No other products besides **6a** were observed in either $^{19}F$ or $^{31}P\{^1H\}$ NMR spectra when the reaction was performed in a PTFE (Teflon) NMR liner, although the $^{19}F$ NMR analysis was hindered by the PTFE absorbance in the aromatic fluorine region of the spectrum. In a regular NMR tube, small amounts (∼10%) of a byproduct were also observed. The byproduct most likely contains a metal-coordinated $HF_2^-$ anion, which appears in the $^{19}F$ NMR spectrum as a small hump at ∼−180 ppm at room temperature and as a broad doublet of doublets at −78 °C. In addition, a small broad signal at 11.5 ppm, expected for $HF_2^-$, also appeared in the $^1H$ NMR spectrum.[16] Furthermore, upon standing of the reaction mixture for several days at room temperature in a regular NMR tube, the signals due to the reactant **2a** started to reappear in the NMR spectra. The $^{19}F$ NMR spectrum of complex **6a**, which can be prepared independently from **2a** and AgF, shows a broad signal at −277.1 ppm due to the platinum-bound fluoro ligand, as well as the signals of the pentafluorophenyl group. In its $^{31}P\{^1H\}$ NMR spectrum, the phosphorus atom trans to the fluoro ligand gives rise to a doublet at 48.1 ppm ($J_{FP}$ = 160 Hz). The X-ray structure of **6a** (Figure 2) shows features similar to those in **2a** except that the Pt(1)−P(2) distance (trans to the fluoro ligand) of 2.1987(19) Å is now shorter than in the parent compound (2.2354(12) Å), indicating the smaller trans influence of the fluoro ligand vs iodide. The Pt(1)−F(4) bond length of 2.035(4) Å is in the right region for a Pt(II) fluoride.[17]

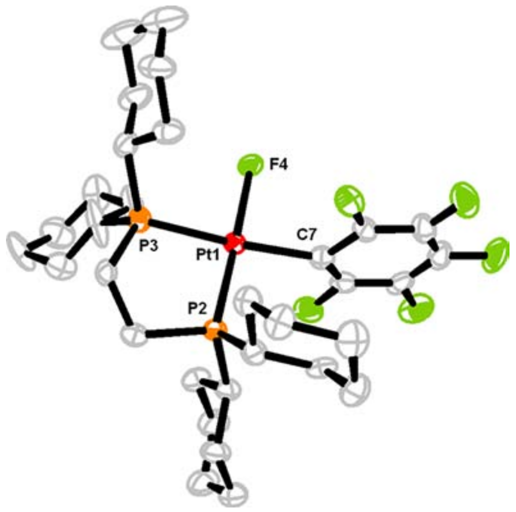
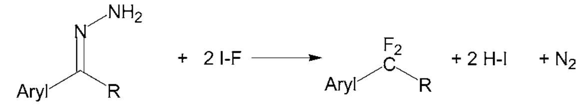


**Figure 2.** X-ray crystal structure of complex **6a**. Hydrogen atoms are omitted for clarity.

As the stoichiometry of the reaction in Scheme 4 suggests the formation of xenon and an I−F species, we decided to check the reaction mixture for the presence of a product with an iodine−fluorine bond in it. Iodine monofluoride is known to form a polymer in dilute solutions[18] and is relatively unstable, giving free iodine and $IF_3$, which in turn decomposes to $I_2$ and $IF_5$.[19] Being a source of a strongly electrophilic iodine, I−F is also known to react rapidly with hydrazones, giving the difluoromethylene compounds, dinitrogen and HI (Scheme 5).[20] To verify the formation of the product(s) containing I−F bond, we treated the solution containing **6a** and the presumed I−F species, prepared at −78 °C, with a slight excess of benzophenone hydrazone. To our delight, instantaneous appearance of a signal at −89 ppm due to the formation of $Ph_2CF_2$ was observed in the $^{19}F$ NMR spectrum, which was confirmed by comparison with the authentic sample of $Ph_2CF_2$. The released H−I converts **6a** to **2a** within seconds (Figure 3), which was verified independently. It is possible that slow production of $I^-$ is responsible for the regeneration of **2a** upon leaving the reaction mixture in Scheme 4 for several days at room temperature.

**Scheme 5**



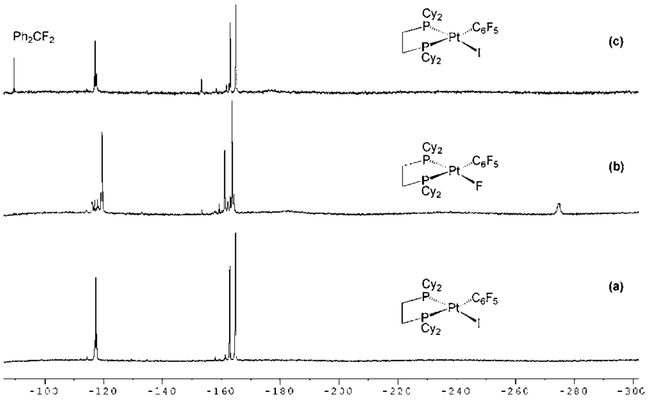


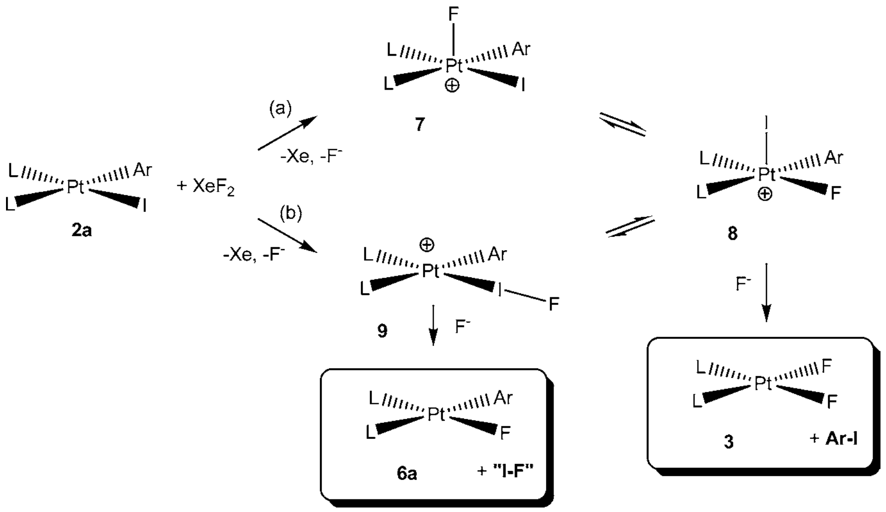
**Figure 3.** The $^{19}F\{^1H\}$ NMR spectrum of: (a) **2a** in $CH_2Cl_2$; (b) after the reaction with $XeF_2$; (c) after the addition of $Ph_2C{=}N{-}NH_2$.

The apparent formation of products with the I−F bond in the reaction between **2a** and $XeF_2$ raises the question about the possible pathways that can be involved in the reaction between $XeF_2$ and aryliodoplatinum(II) complexes. The most commonly anticipated reaction direction involves oxidative addition of an $F^+$ to a Pt(II) center in **2a** that gives the coordinatively unsaturated Pt(IV) species **7** (path a, Scheme 6).[21,22] The latter may undergo the isomerization that puts the iodo ligand in the axial position (**8**) and form products of the subsequent C−I reductive elimination. Another plausible mechanism (path b) includes direct attack of $XeF_2$ at the coordinated iodo ligand in **2a**[23,24,12] to form an I-coordinated Pt(II) I−F complex **9** which can subsequently produce either **6a** and free I−F as a result of F-for-I−F ligand substitution, or **8** as a result of intramolecular oxidative addition of I−F to the Pt(II) center.

The second mechanism (path b) allows one to account for the observed behavior of complexes such as **2a** that are too sterically congested and/or electron poor to accept an electrophilic attack by $XeF_2$ onto the metal atom (path a). In such a case, an attack by $XeF_2$ onto the much more sterically accessible iodo ligand in **2a** (path b) may lead to the accumulation of **6a** and I−F at low temperatures if it occurs at a faster rate than that of the oxidative addition of I−F to form **8**.

To check the viability of path b for complex **2a** we performed a crossover experiment. A fresh mixture of **6a** and I−F species was prepared in the reaction between **2a** and $XeF_2$ and was kept at −78 °C. Then it was combined with an electron-richer aryl fluoride complex (dcpe)Pt(4-$FC_6H_4$)F, **5a**. With I−F species present in the former mixture we expected formation of *p*-

Scheme 6



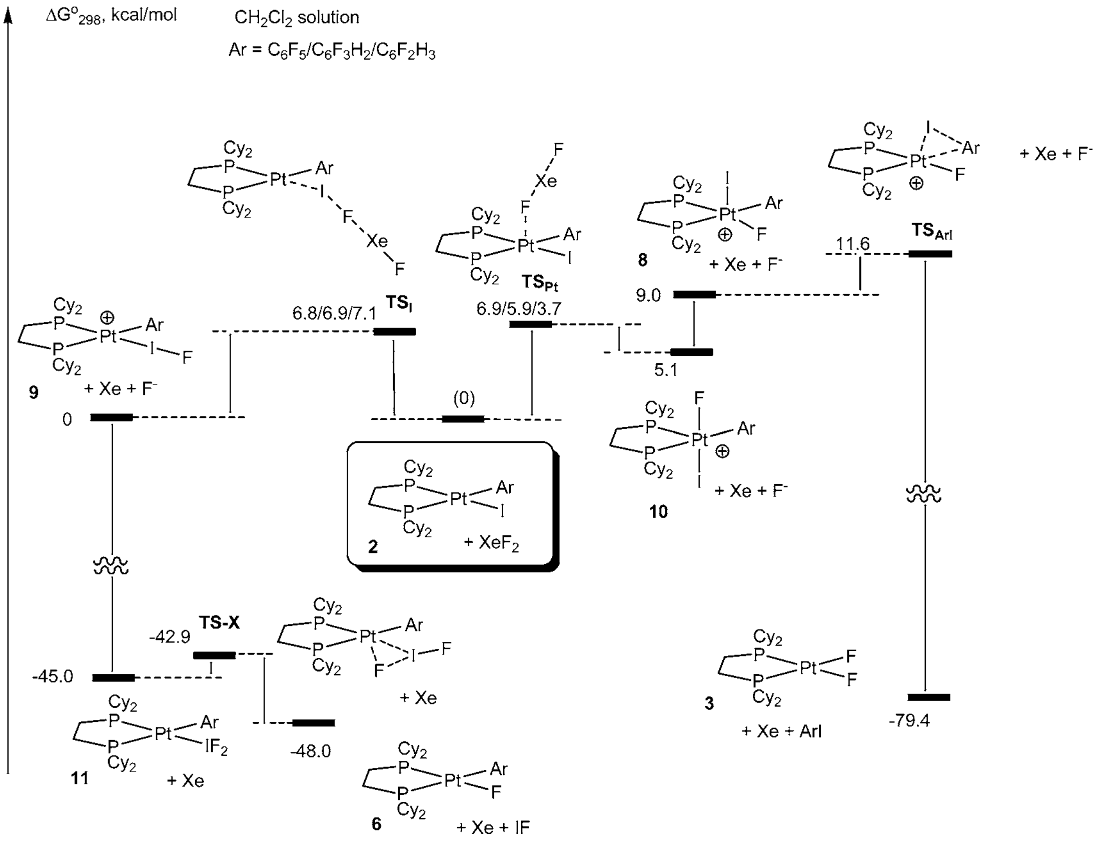


**Figure 4.** DFT calculated Gibbs energy profile for reaction between complex **2** and $XeF_2$ in dichloromethane solutions, $\Delta G^{o}_{298}$, kcal/mol.

fluoroiodobenzene as a result of the reaction between I—F and **5a**. Indeed, *p*-fluoroiodobenzene formed instantaneously along with **3**, thus supporting the viability of path b.

In addition, we also prepared iodine monofluoride by reacting $I_2$ with $F_2$ at −78 °C.[20] The addition of a small amount[25] of the polymeric I—F to a solution of **5a** in $CH_2Cl_2$ at this temperature led to the formation of **3** and $4\text{-}IC_6H_4F$.[26]

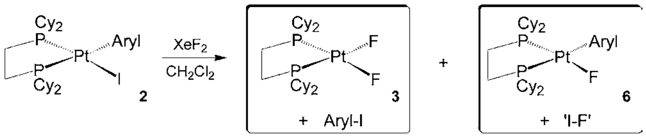
Analyzing the reactivity of sterically bulky mesityl complex **1e** and electron-poor complexes **1f** and **1g** that all undergo an exclusive aryl-I elimination reaction upon treatment with $XeF_2$, we propose that the fluoro substituents present in the aryl ligand play a crucial role in directing the attack of $XeF_2$ at the iodo ligand in Pt(II) aryl iodo complex **2a**. To check this hypothesis, we studied fluorination of polyfluorophenyl complexes **2b**−**d** with $XeF_2$. Importantly, the reaction outcome was found to be dependent on the number and position of the fluoro substituents in the aromatic ring. With 2,4,6-trifluorophenyl complex **2b** and 2,6-difluorophenyl complex **2c**, both complex **3** (along with the corresponding aryliodide) and complex **6** were obtained in a 4:6 and 7:3 ratio, respectively, whereas with 2,4-difluorophenyl complex **2d**, only the aryl-iodide reductive elimination products were observed. The presence of "I—F" in the reaction mixture of **2b** and $XeF_2$ was also evident from the formation of $Ph_2CF_2$ observed upon combination of this mixture with $Ph_2C{=}N{-}NH_2$. Thus, the presence of at least *two* ortho-fluoro substituents was crucial for directing the electrophilic attack of $XeF_2$ at the iodo ligand leading to the formation of **6** and I−F species.

The effect of the ortho-fluoro substituents at the aryl ligand on the reactivity of late transition metal complexes has previously been reported.[27] In particular, it was demonstrated that, in a rhodium complex, two ortho-F substituents increase the barrier for the aryl-H reductive elimination by ~5 kcal/mol compared with the single fluorine.[28]

To get a better understanding of the reactivity of polyfluorophenyl complexes **2a**, **2b**, and **2c** toward $XeF_2$, both reaction paths a and b shown in Scheme 6 were analyzed using DFT calculations for dichloromethane solutions (Figure 4).[29]

For the pentafluorophenyl complex **2a**, path a includes the electrophilic attack of $XeF_2$ at the $Pt^{II}$ center via the transition state $\mathbf{TS_{Pt}}$ (6.9 kcal/mol) to form intermediate **10** (isomer **7** in Scheme 6 could not be located on the potential energy surface). The intermediate **10** can isomerize to transient **8**, leading to facile reductive elimination of $C_6F_5$−I. The corresponding transition state $\mathbf{TS_{ArI}}$ is the highest energy point (11.6 kcal/mol)[29] on the reaction energy profile. Path b for complex **2a** includes a relatively low-energy transition state $\mathbf{TS_I}$ (6.8 kcal/mol) corresponding to the electrophilic attack of $XeF_2$ at the iodo ligand in **2a**. This transition state leads to an I-coordinated I−F $Pt^{II}$ complex **9** that, upon reaction with fluoride anion, can give rise to the observed **6** and free I−F. Another possible site of the attack of fluoride anion at the intermediate **9** might include the iodine atom. In this case the resulting intermediate is the $Pt^{II}$−I-coordinated difluoroiodide complex (dcpe)Pt-$(C_6F_5)$($\kappa$*I*-$IF_2$), **11**; this reaction direction is also very favorable (−45.0 kcal/mol). Complex **11** can reductively eliminate I−F with a very low activation energy of 2.1 kcal/mol relative to that of **11** to form complex **6**. Either of the two reaction mechanisms leading to **6** and I−F may be operational. The outcome of the competition between these two reactions will depend on the relative height of the activation barriers, including partial desolvation of the fluoride anion and its subsequent coordination to either the $Pt^{IV}$ or I center.[29] Importantly, based on very similar energies of $\mathbf{TS_I}$ and $\mathbf{TS_{Pt}}$, both reaction directions, fluorination at the iodine atom and at the $Pt^{II}$ center, look almost equally probable. Taking into account a possible error associated with DFT calculations, this prediction agrees satisfactorily with the experimental data given in Scheme 7. Interestingly, the formation of an F-coordinated I−F complex (dcpe)Pt$(C_6F_5)$($\kappa$*F*-IF), **12** can also occur as a result of F−I bond reductive elimination from intermediate **8** but with the Gibbs activation energy of 12.4 kcal/mol (see Supporting Information).

Scheme 7



| | Complex | Products ratio | |
|---|---|---|---|
| Aryl= | $C_6F_5$ (**2a**) | 0 | 100 |
| | 2,4,6-$F_3C_6H_2$ (**2b**) | 42 | 58 |
| | 2,6-$F_2C_6H_3$ (**2c**) | 70 | 30 |
| | 2,4-$F_2C_6H_3$ (**2d**) | 100 | 0 |

Finally, the barriers corresponding to the electrophilic attack of $XeF_2$ at the $Pt^{II}$ center and the iodo ligand in complexes **2b** and **2c** were also found. As the number of fluorine atoms in the aryl ligand decreases, the Gibbs activation energy for the attack of $XeF_2$ at the iodine atom remains almost the same (6.8, 6.9, and 7.1 kcal/mol for **2a**, **2b**, and **2c**, respectively), whereas the barrier corresponding to the attack of $XeF_2$ at the $Pt^{II}$ center decreases noticeably (6.9, 5.9, and 3.7 kcal/mol for **2a**, **2b**, and **2c**, respectively), reflecting well the experimental trend shown in Scheme 7.

## ■ CONCLUSION

We provided strong evidence for the existence of an alternative pathway of electrophilic fluorination of organometallic iodo Pt(II) complexes with $XeF_2$, in addition to the commonly accepted pathway including electrophilic attack of $XeF_2$ at the $Pt^{II}$ center. The new reaction pathway involves the unprecedented (for organometallic chemistry) formation of an I−F bond via the direct fluorination of the coordinated iodo ligand. Evidence for the generation of such a bond was obtained from the reactions between the (dcpe)Pt(Ar)I complexes **2a**−**c** and $XeF_2$, where the aryl ligand of complex **2** bears two ortho-fluoro substituents. In the case of the complex **2a** containing the pentafluorophenyl ligand, the formation of (dcpe)Pt$(C_6F_5)$F and putative I−F was the only documented reaction pathway. As the steric environment at the Pt center should be similar for all three complexes, electronic effects seem to play the major role in determining the reaction outcome. DFT calculations are in qualitative agreement with the experimental data and show the trend of the diminishing activation barrier corresponding to the attack of $XeF_2$ at the $Pt^{II}$ center in the series **2a** > **2b** > **2c**, whereas the activation barrier corresponding to the attack at the iodine atom remains unchanged.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental and computational details; X-ray crystallographic data for complexes **1e**, **2a**, **b**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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